

HIGH TEMPERATURE PROCESSING OF LINE-PIPE STEELS

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Abstract

It has been determined that by reducing the carbon content of line-pipe steel to about 0.03% many property improvements are achieved such as excellent toughness, ductility and ease of welding as well as reduced segregation including the slab centerline regions, necessary to guarantee resistance against sour media. Furthermore, lower carbon contents increase the niobium carbide solubility and permit the use of higher niobium contents than these traditionally used. Niobium contents up to 0.10% have recently been adopted in these low carbon pipe steels. With higher niobium contents austenite processing can be carried out at higher rolling temperatures. Additional strength increases are observed due to niobium's role in retarding the transformation to ferrite, thus promoting a higher volume fraction of bainite, and by forming NbC precipitates in ferrite. This concept is ideally suited to produce high strength via accelerated cooling, but one has to balance the amount of alloying elements with the cooling rate to guarantee the demanded strength level for the considered plate thickness. These alloy designs are not only suitable for producing high strength sour gas resistant pipes, but the approach also allows the production of pipes with high toughness on mills not capable of withstanding high rolling forces and additionally on Steckel mills, where coiling the sheetbars is often the limiting factor during severe thermomechanical rolling. Another interesting application is for the substrate of clad pipe, where the corrosion resistance of the cladding requires high finish rolling temperatures, which would otherwise result in insufficient toughness in the base metal.

Introduction

Thermomechanical rolling is used to maximise grain refinement and thus achieve both higher strength and toughness. It is the standard means to produce plate or strip for high strength large diameter line pipe to fulfil the safety requirements of the pipeline industry. Thermomechanical rolling is characterised by processing austenite in the temperature region of non-recrystallisation, which results in an enhanced number of nucleation sites for the γ to α transformation. Austenite grain development during thermomechanical rolling is shown schematically in Figure 1. However, there are metallurgical situations or facility limitations, where processing at temperatures of the metastable austenite is not feasible or advisable.

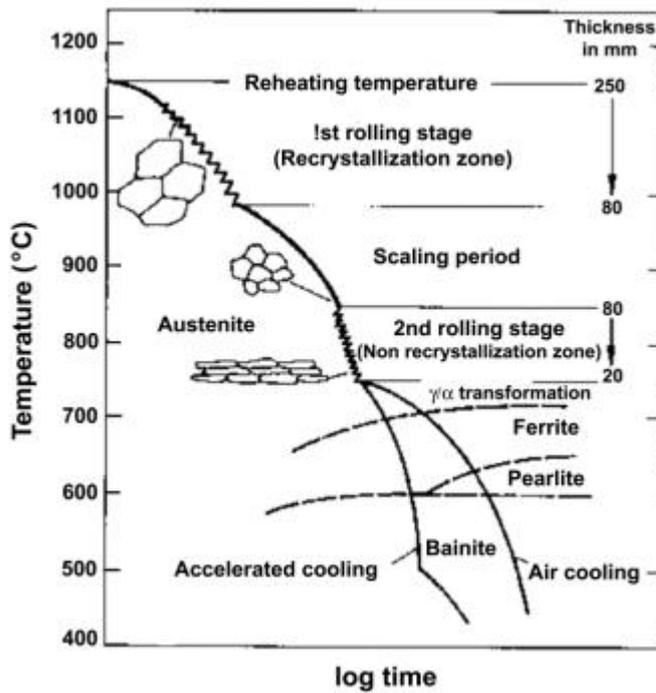


Figure 1: Schematic representation of the thermomechanical rolling process

Fundamental Considerations for the Alloy Design

When the amount of solute niobium is increased, retardation of austenite recrystallisation is observed at significantly higher temperatures, Figure 2 (1), thereby allowing the benefits of thermomechanical rolling to be achieved at higher temperatures. Low carbon contents and the fixing of nitrogen with titanium, an element with a higher affinity for nitrogen than niobium, prevent niobium carbonitride formation and allow the higher niobium content to be easily dissolved during reheating of the slabs, Figure 3 (2,3). In this paper examples of such steels having about 0.03% percent carbon, 0.09/0.10% niobium and Ti/N treatment, specifically designed for high temperature processing (HTP), will be called HTP steel.

The selected titanium addition close to the stoichiometric ratio [% Ti = 3.42 x % N] has an additional benefit, since it combines with nitrogen at relatively high temperatures. The TiN compound remains stable at high temperature during reheating and prevents impairment in toughness due to 'free nitrogen' N_f , according to the correlation:

$$\text{FATT} = k + v\% N_f \quad (1)$$

(In this equation FATT is the 50 % ductile to brittle fracture appearance transition temperature measured in the Charpy V notch impact test). The effect of free nitrogen is especially important with regard to the toughness in the heat affected zone of a weldment.

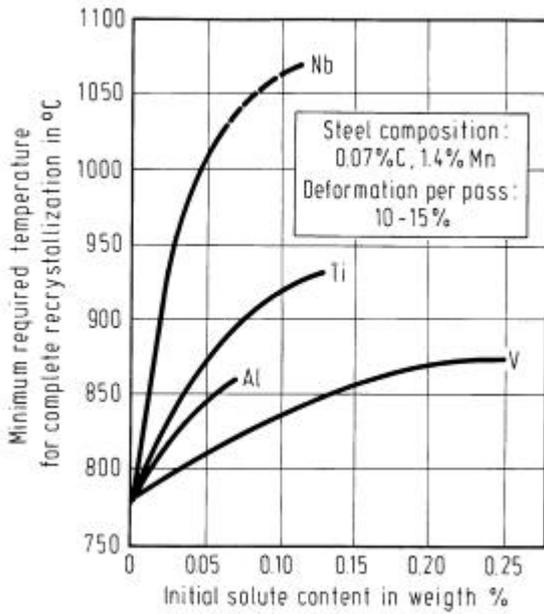


Figure 2: Retardation of recrystallisation by microalloying.

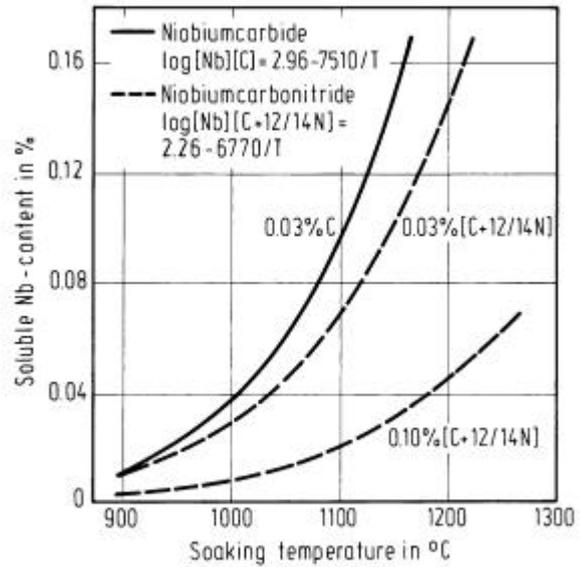


Figure 3: Solubility of niobium carbide and carbonitride respectively.

Besides its direct influence on the solubility product of the niobium compounds, the low carbon content provides better toughness and ductility. This is especially relevant in clean steels, which are characterised by very small amounts of oxides and sulphides preferably in a globular form (5) - and high purity is a prerequisite in modern high strength low alloy (HSLA) steel. Typical sulphur levels in pipe steel are < 0.005 % but in case of steels requiring resistance against hydrogen induced cracking (HIC) the level may be as low as 10 ppm maximum. In order to convert the remaining oxides and sulphides to a globular form, calcium treatment is commonly applied. To be effective the calcium addition has to be above the stoichiometric ratio of $\text{Ca/S} = 1.25$ and a ratio of around 2 is typical for low sulphur steels.

Furthermore, the low carbon content reduces the tendency for segregation, as schematically demonstrated in Figure 4: Most harmful in medium carbon steels is the interdendritic enrichment during the peritectic reaction, where an additional shrinkage occurs due to the formation of face centred cubic austenite from the body centred cubic delta ferrite. Since liquid steel is also present in this reaction and is naturally enriched in alloy content, it becomes concentrated and later is trapped in the interdendritic pools. By further lowering carbon content below the threshold value of 0.09%, dendritic segregation is also reduced by both - the reduced solidification interval and the bigger delta ferrite interval, which facilitates homogenisation because the diffusion coefficient of solute elements in ferrite being 100 times higher to that of those in austenite.

The improvement in properties of weldable steel grades began with the substitution of manganese for carbon (6). A higher manganese to carbon ratio leads to better toughness at equal strength. As a result manganese is the most commonly used solid solution strengthening element added to HSLA steels. Based on the above discussed, a carbon level of 0.03% and a manganese level of around 2% would be needed to guarantee the strength level of X 70. However, in case resistance against hydrogen induced cracking (HIC) is also required, the manganese content must be limited in order to avoid the formation of hard microstructural

constituents. The tolerable manganese content increases with lower carbon levels as shown in Figure 5 (7) but should not be higher than about 1.7 % Mn for the 0.03% carbon level.

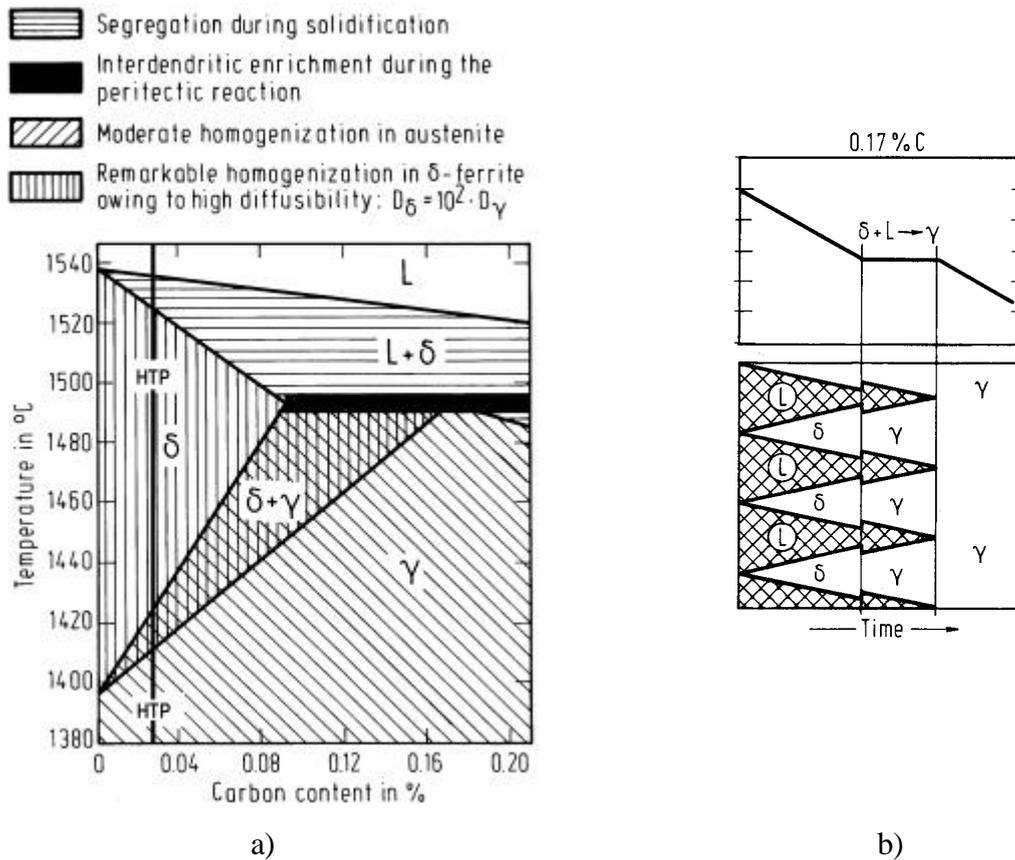


Figure 4: a) Part of the Fe-C diagram with classification of the segregation Severity and b) Schematic demonstration of the peritectic reaction.

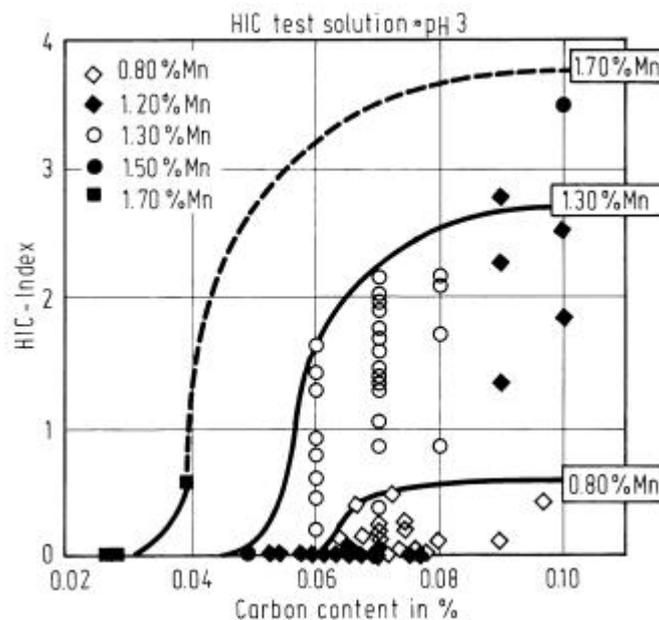


Figure 5: Influence of carbon and manganese on HIC resistance.

In order to compensate for the reduced strength due to manganese restrictions other solid solution strengthening elements have to be added. Elements are preferred, which are readily

available and have no detrimental effect on HIC resistance. It is well known that additions of copper, but also chromium and nickel reduce the corrosion rate under medium severe sour conditions and thus reduce the hydrogen charging rate at the pipe surface, Figure 6 (8).

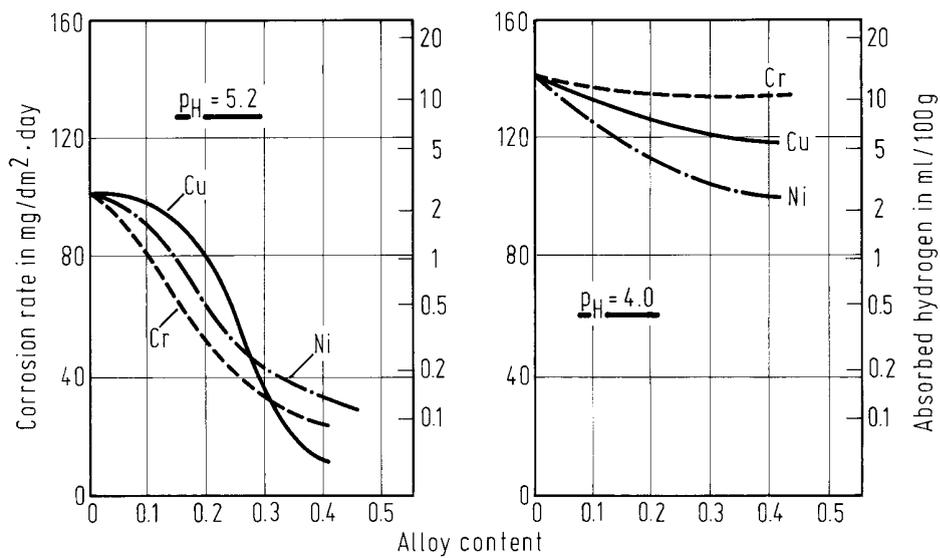


Figure 6: Influence of alloying elements on steel corrosion and hydrogen absorption in wet H₂S environment.

Processing-Microstructure Relationships

Following the above described concept a demonstration heat was produced in Japan in 1983 and was processed in rolling mills of thirteen different companies using a wide variety of rolling regimes (9). The chemical composition relied on 0.03% carbon, 0.10% niobium, titanium (0.014%) to fix the low nitrogen content (0.0035%) and calcium treatment of the low sulphur (0.0008%) steel. The latter was required to ensure good sour gas resistance. For the same reason the addition of manganese was restricted to about 1.75 % and other alloying elements such as Cu+Cr+Ni were added, in total 0.75 %. The microstructural development resulting from the various processing conditions are discussed along with data from a HTP steel melted in Mexico, having a 0.25% lower manganese content, the rest of the alloy contents being similar. This alloy design was applied in a 36" x 22 mm X 70 sour gas resistant offshore pipeline (10), but many data were also developed with trial production at various companies.

Slab Structure – Macro Etch

Deep etched slab samples show a complete surface to centre columnar crystal structure without any equiaxed zone in the slab centre. Such macroscopic investigations also show very little segregation in the centreline region with only occasional shrinkage holes.

This low degree of segregation is confirmed by chemical analyses presented in Figure 7. The segregation ratio of the most relevant alloying element manganese is very low, amounting to a ratio in the slab centre region of 1.06 at the most with no value above 1.90 percent manganese detected in the 1.8 % Mn steel. This is an extremely good result, since a manganese segregation coefficient of two is commonly detected in traditional HSLA steels having about 0.10% to 0.12% carbon and 1.30% to 1.50% manganese. This result is given together with the data of carbon and niobium segregation in Figure 7.

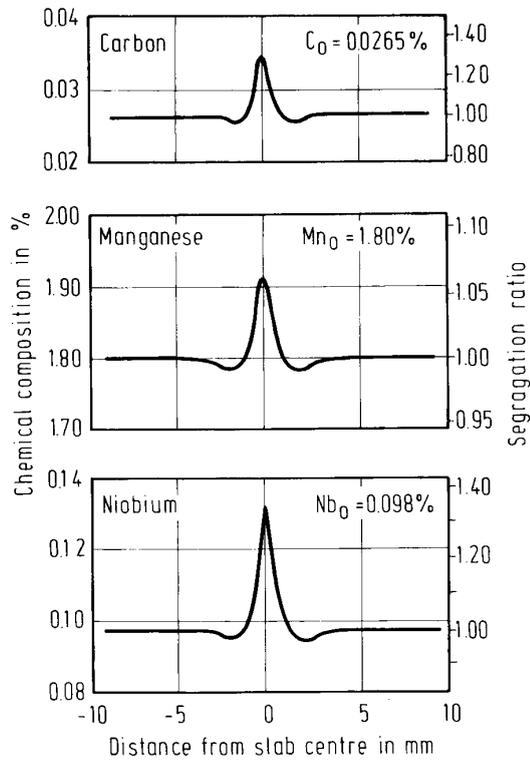


Figure 7: Segregation of carbon, manganese and niobium in the HTP slab.

Slab Structure – Electron Microscopy

Two kinds of particles were observed in the continuously cast slabs – Figure 8:

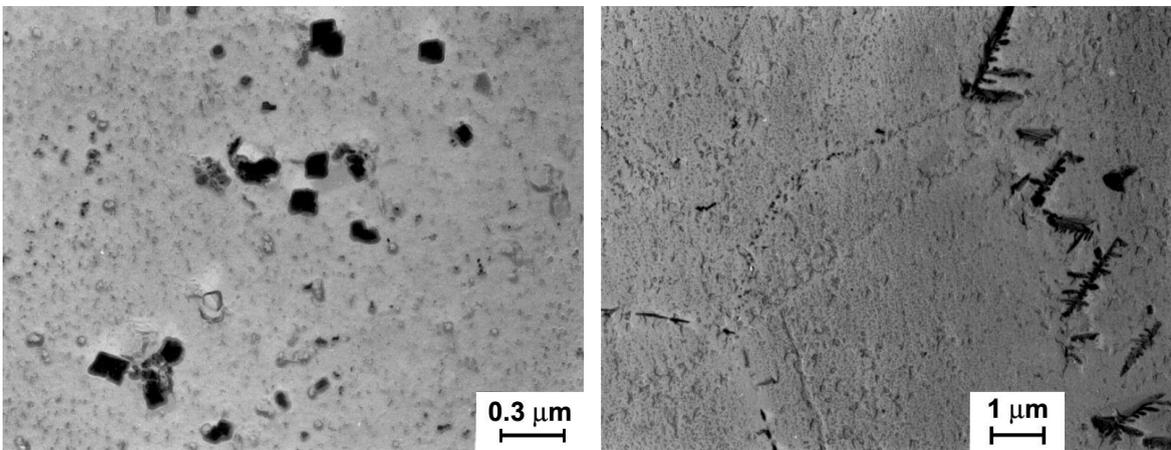


Figure 8: TEM observations in HTP slabs showing cuboidal and dendritic precipitates.

- Fine cuboidal particles of 200 nm maximum size, randomly dispersed in the matrix, and exhibiting signs of continuous growth. STEM investigations confirm, that these particles are titanium rich and, as predicted by thermodynamic calculations, are formed at rather high temperatures. Thus they are also stable at high reheating temperatures. In contrast to observations in many other titanium treated HSLA steels no large ‘TiN’ cuboids, rather ineffective for grain refinement, were detected. The relatively small particle size is a result of the low nitrogen and understoichiometric titanium addition, which prevents TiN formation in the liquid steel or during solidification.
- Dendritic particles decorating the prior grain boundaries almost independent of the location of the cuboidal particles. Such fern like dendrites are several microns long and

are unstable even at 1050 °C. The chemical analysis indicates, that these are niobium rich particles, which contain about 20% titanium in the core and 15% near the surface.

Recrystallisation Stop Temperature

The recrystallisation stop temperature T_{NR} has been determined by simulating hot rolling on a hot torsion machine: true strain per pass = 0.25, interpass time = 30 s, cooling rate = 1 °C/s (11). The data in Figure 9 confirm 1060 °C as T_{NR} for this steel, a temperature, which corresponds to the onset of strain induced precipitation of niobium carbides in austenite. As a result, all deformation below this temperature promotes austenite grain elongation, which is the essence of thermomechanical rolling. Even when aiming for a total deformation of three to four times final thickness in this temperature range, the finish rolling temperature for HTP steel can be more than 100 °C higher than typical for conventional pipe steels. This allows reduced rolling forces and adds to mill productivity.

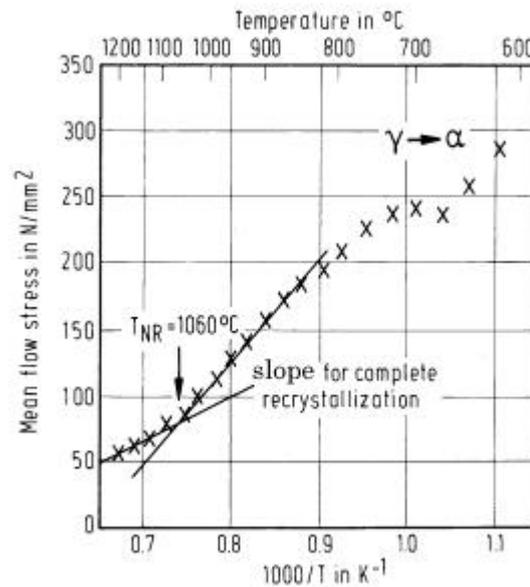


Figure 9: Mean flow stress of HTP steel at different deformation temperatures.

Status of Niobium in Plate and Strip

Since the slab reheating temperature is typically 1150 °C or higher, it can be assumed, that all the dendritic 'NbC' precipitates will be dissolved according to the solubility product shown in Figure 3 and therefore almost all the niobium should be in solid solution at the commencement of rolling. During austenite conditioning a portion of the niobium will be precipitated as strain induced carbonitride or carbide on dislocations. Using chemical extraction techniques described elsewhere (9), the undissolved and the strain induced austenite precipitates remain in the filter residue, while niobium in solid solution and the fine ferrite precipitates will be dissolved. This technique allows one to investigate the status of niobium at the finish rolling temperature.

Results of chemical extraction studies in relation to the equilibrium condition are shown in Figure 10. Conventional pipe steel, processed on a plate mill with a typical finish rolling temperature below 800°C, allows only a small portion of niobium to remain in solid solution and the amount of 'soluble' niobium is close to the equilibrium condition. A higher 'soluble' niobium content of almost 0.02% is observed in hot strip, where the final deformation steps are

continuous and feature higher rolling speeds and shorter interpass times as well as a finish rolling temperature about 100°C higher than for plate rolling. In contrast the HTP steel shows a 'soluble' niobium content as high as 0.04% for typical finish rolling temperatures in a plate mill, with even higher values for hot strip processing.

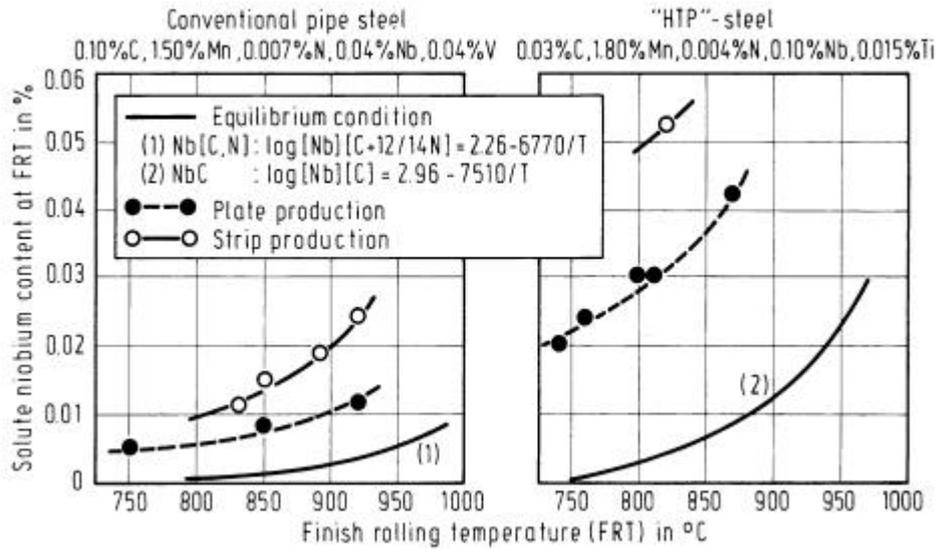


Figure10: Niobium in solid solution at different finish rolling temperatures for two pipe steels (determined by the chemical extraction method).

In the HTP steel three distinct kinds of particles have been found as follows:

- Large (300 nm) cuboid particles, more or less uniformly distributed
- Many cuboid and round shaped incoherent particles of about 30 nm diameter
- Very fine precipitates of 2 to 8 nm homogeneously precipitated within the ferrite grains

Examples of the later two kinds of precipitates are given in Figure 11.

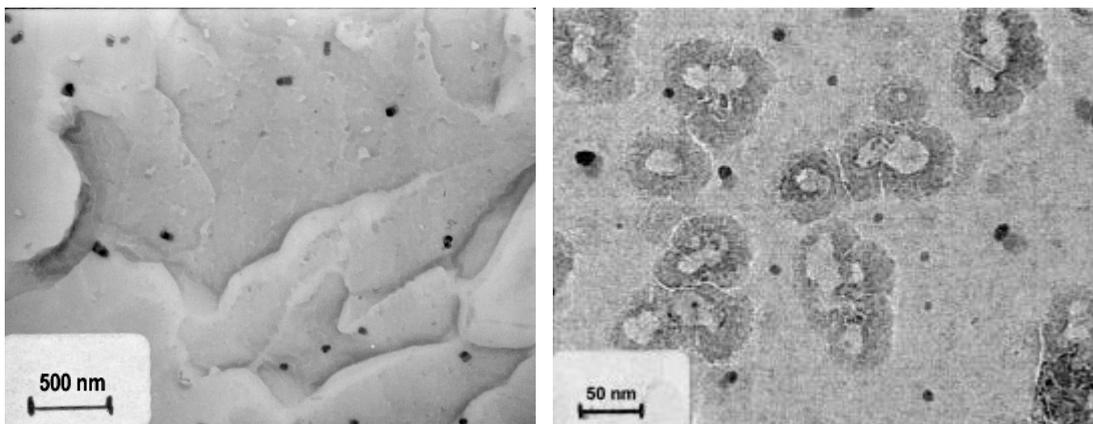


Figure 11: Incoherent austenite precipitates and fine ferrite precipitates.

The determination of chemical composition and lattice parameters of the incoherent precipitates in the filtration residue indicate that the coarser particles are close to a pure TiN, while the finer particles are almost pure NbC, Figure 12. The coarse 'TiN' particles are similar to those in the slab. They were not dissolved during reheating and therefore have some small influence on the reheated austenite grain size. The finer 'NbC' particle fraction was formed by strain induced

precipitation during austenite processing and is responsible for retarding recrystallisation. Other researchers have also found that these two distinct particle types exist (12), which confirms that Ti/N treatment of HSLA steel can enhance niobium's effectiveness.

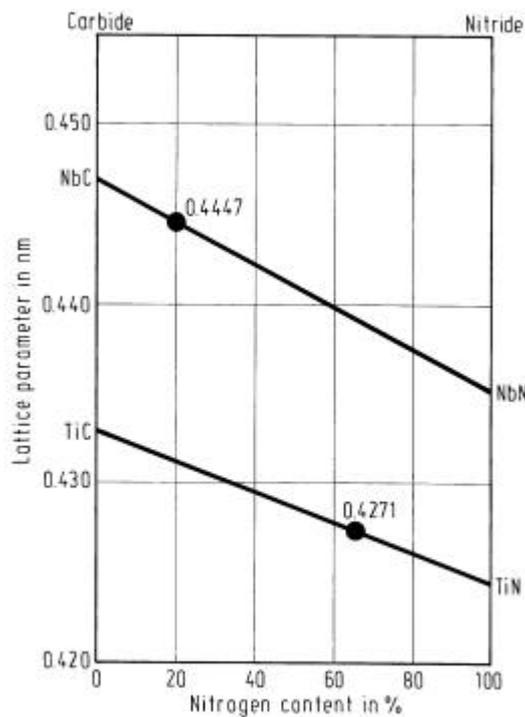


Figure 12: X-ray lattice parameters of carbo-nitrides in extracted residue of 0.03 % C – 0.10 % Nb, titanium – treated plates.

Niobium in solid solution at the finish rolling temperature is available for the formation of niobium carbide precipitates in ferrite, which have the appropriate size for additional strength increase via precipitation hardening and an example has been shown above. Additionally, niobium in solid solution has also an effect in reducing the γ/α transformation, as will be discussed below.

Transformation Behaviour

The CCT diagram of the HTP steel after deformation in the metastable austenite region is shown in Figure 13. As result of the steel's low carbon content the microstructure will not show any pearlite at typical cooling rates of plate. Air cooling at approximately 1 °C/s results, after thermomechanical rolling, in a microstructure consisting almost completely of polygonal ferrite with a very small percentage of low carbon bainite, often referred to as acicular ferrite. The CCT diagram of this steel shows clearly that no carbon-rich martensite islands are formed. This distinguishes it from other low carbon bainitic grades, especially at rather slow cooling rates (13). With higher cooling rates the volume fraction of bainite increases and at 15 °C/s, typical for the cooling rate in accelerated cooling 20 mm plate, at least 50% of the microstructure is bainitic, the balance being polygonal ferrite. The microstructure of these two phases is shown in Figure 14 which underlines the higher dislocation density and the smaller effective grain size in the bainite.

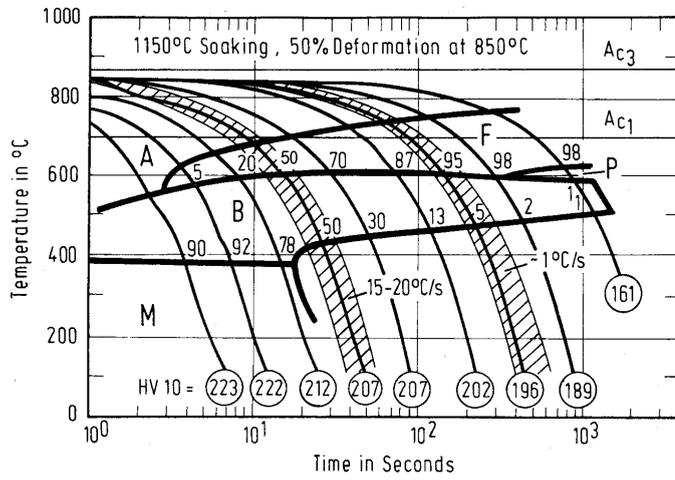


Figure 13: Deformation CCT diagram of HTP steel.

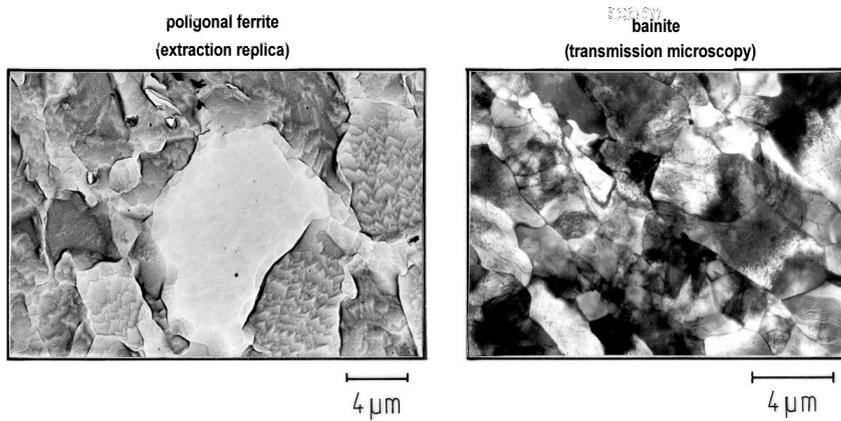


Figure 14: Typical microstructures of ferrite and bainite in HTP steel.

As a consequence of its relatively large atom size, niobium in solid solution retards the γ/α transformation. Quantitative metallography results for HTP plate and skelp with various soluble niobium contents are shown in Figure 15. For the air cooled plates the amount of bainite increases with a higher fraction of solute niobium at the finish rolling temperature.

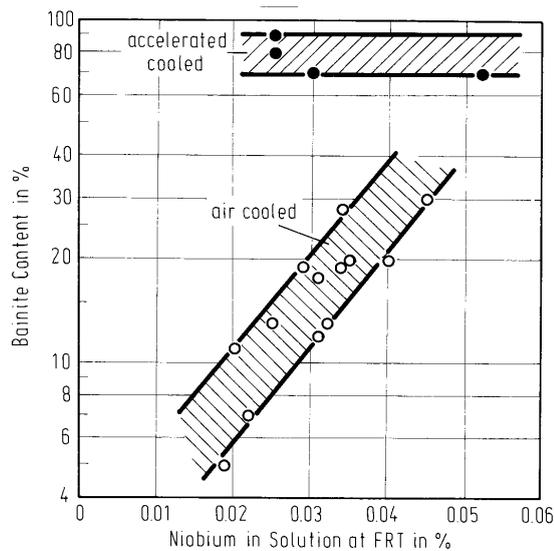


Figure 15: Influence of niobium in solid solution at the finish rolling temperature on the volume fraction of bainite in air cooled and accelerated cooled HTP plate.

Processing-Properties Relationships

For 0.03 % C – 0.10 % Nb – 1.75 % Mn - HTP steel

The mechanical properties achieved with the above mentioned demonstration heat (9) are summarised in the following figures:

The results shown in Figure 16 were achieved with a simple two stage rolling schedule including one delay after roughing and before starting final rolling in the non-recrystallisation region at about 900 °C with a finishing rolling temperature of 820 °C. This finish rolling temperature is about 100 °C higher than for conventional thermomechanically processed pipe plates. The tensile properties are barely sufficient to satisfy X 70 grade requirements, when the final deformation starts with a transfer bar having a thickness of three times plate thickness. However increasing the finish rolling severity to 3.5 times final thickness, improved yield, tensile strength and better toughness are obtained. The Charpy-V notch and the Batelle drop weight tear test (BDWTT) versus testing temperature curves are shown in Figure 17, underlining the excellent toughness which is obtained in such a low carbon alloy design.

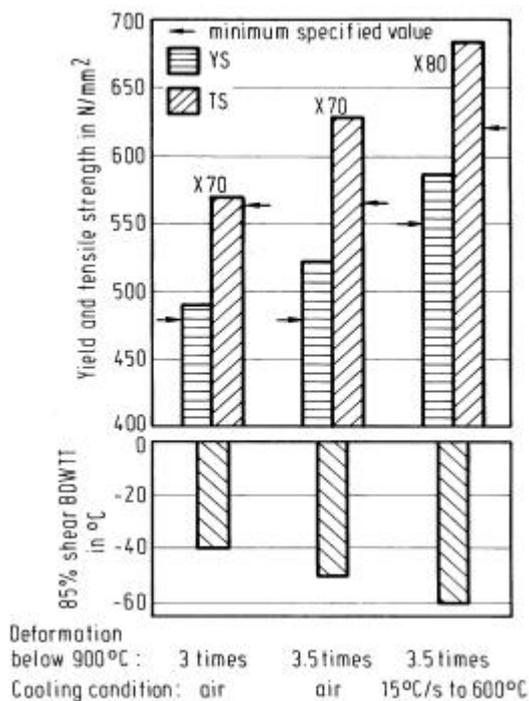


Figure 16: Properties of 18 mm HTP plates containing 1.75 % Mn as a function of finish rolling and cooling conditions; finish rolling temperature = 820 °C

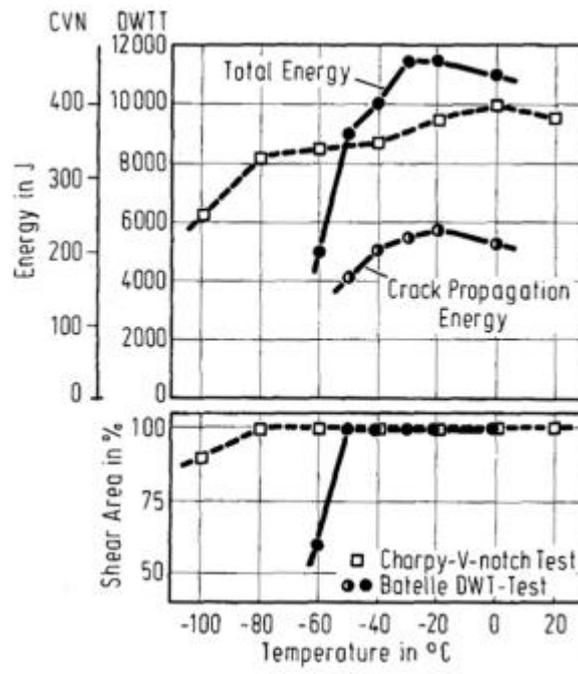


Figure 17: Results of CVN and BDWTT impact test versus testing temperature of 18 mm HTP plate (FRT = 820 °C)

With the higher cooling rate of 15 °C/s typical for accelerated cooling, the transformation into a low carbon bainitic microstructure is promoted. Both, the finer effective grain size and the higher dislocation density of the bainite add to strength increase and the pipe plate thereby reaches X 80 properties. Also a further toughness improvement is achieved as a result of the finer effective grain of the bainite constituent.

There is an optimum cooling stop temperature after accelerated cooling of approximately 500 to 550 °C, which is illustrated in Figure 18. At higher cooling stop temperatures the bainite

volume fraction is not maximised and at lower cooling stop temperatures some martensite particles are detected, which reduce the yield strength by internal stresses. The property combinations reported above are obtained for a wide range of different plate thickness, which is of utmost importance, since new pipeline projects offshore are being laid in the greater depth and may require wall thickness in excess of 40 mm. The data presented in Figure 19 indicate, that X 70 properties in combination with excellent toughness are obtained with this alloy design. Accelerated cooling after thermomechanical rolling is very helpful to reach this goal, even when considering that the cooling rate is naturally lowered with increasing thickness).

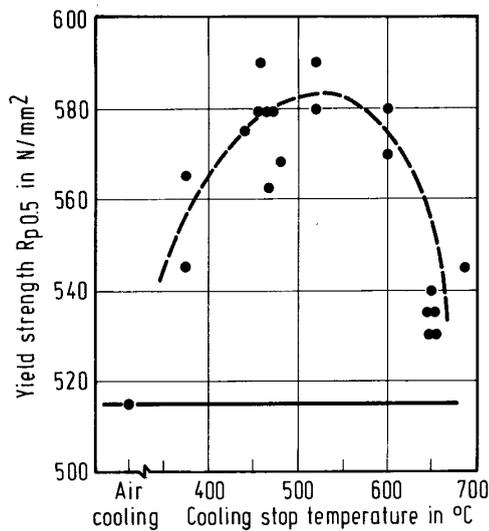


Figure 18: Influence of cooling stop temperature on the yield strength of 18 mm plate

Heating temp.: 1200°C, finishing temp.: 800°C
Accelerated cooling: cooled to 500°C with 8-14 °C/s

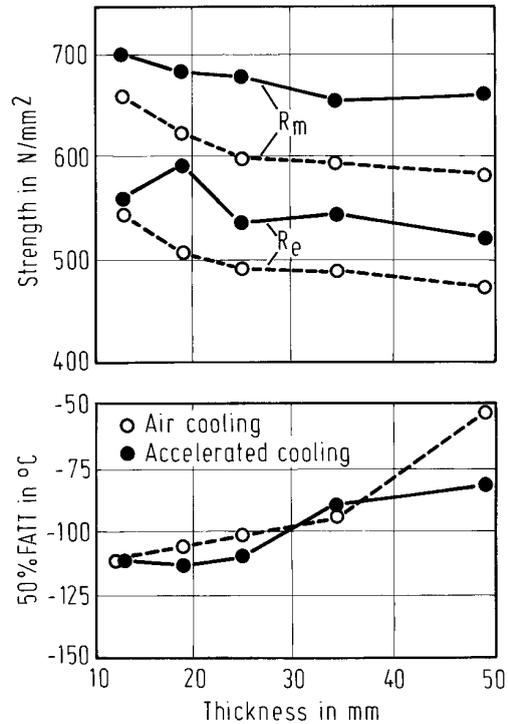


Figure 19: Mechanical properties of HTP plates with different thickness.

While grain refinement by more intensive thermomechanical rolling and/or a higher volume fraction of bainite with its finer effective grain size improves both - strength and toughness of the steel - the effective usage of the precipitation hardening potential of HTP steel additionally increases strength with only limited deterioration in toughness, Figure 20.

A strength increase of 40 to 50 MPa is achieved in both air cooled and accelerated cooled material, if slow cooling is applied after transformation start is reached. This allows the precipitation of NbC to become more complete. The benefit of a reduced cooling speed is achieved naturally in hot strip production, where the material is coiled and is also often used in plate production, when plates are piled up for effective hydrogen removal.

As a consequence of the low carbon content, the transformation in HTP steel starts at comparably high temperature. Thus the possibility exists at typical finish rolling temperatures to add additional strength by increasing the dislocation density in the newly formed ferrite as a result of rolling in the two phase region $\alpha+\gamma$. The yield and tensile strength increase with higher deformation (lower finish rolling temperature) in the two phase region.

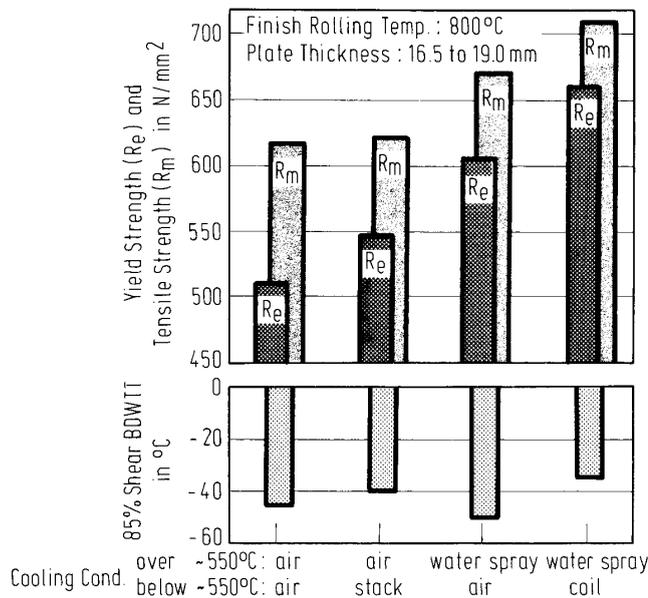


Figure 20: Influence of cooling regime on the mechanical properties of HTP plate/skelp.

For 0.03 % C – 0.10 % Nb – 1.50 % Mn HTP Steel

Data for the 1.75 % Mn containing HTP steel are compared with results for a 1.50 % manganese steel in Figure 21. As a result of the lower manganese content the ferrite transformation starts at about 830 °C and one can achieve X 70 properties with a finish rolling temperature of about 750 °C. Even though this is a finish rolling temperature similar to that used for normal X 70 production, one still can make use of the other outstanding benefits of this alloy design, such as its excellent toughness, ductility, weldability and reduced segregation tendency. In this context the toughness of an intercritically rolled X 70 plate from the low manganese HTP steel should be reported (15); those plates show 85 % shear area in the BDWTT at around – 50 °C and the Charpy-V-notch impact energy is above 300 J down to a testing temperature of < - 80 °C.

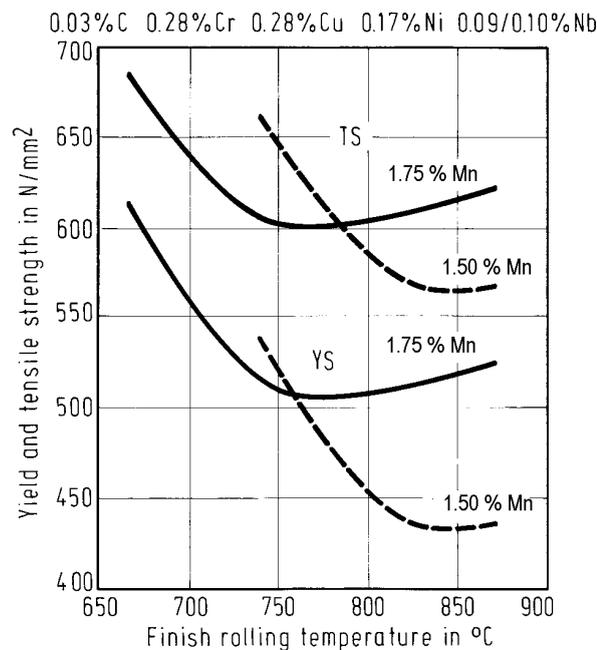


Figure 21: Tensile properties of air cooled HTP plates as a function of finish rolling temperature and the manganese content.

Also evident is the observation, that for air-cooled material, finish rolled in the metastable austenite region, this alloy content is not in itself sufficient to guarantee high strength in the final pipe (14). The influence of various processing conditions on the mechanical properties of this steel type are summarized in Figure 22: When using air-cooling and a final deformation rate of three times final thickness just X 52 properties are achieved in the plate and even with a final deformation of four times only X 60 is obtained. A slightly higher cooling rate of 9 °C/s to a cooling stop temperature at around 600 °C produced a certain percentage of bainite, which increases the tensile properties to the X 70 level. The limits of this approach have been defined and they indicated that X 70 plate properties could be obtained with accelerated cooling of 3.5 °C/s, when the manganese content did not drop below a value of 1.40 % (16). The above discussion relates to plate properties, however after pipe forming the 22.4 mm plate increased in strength and X 70 properties were comfortably achieved.

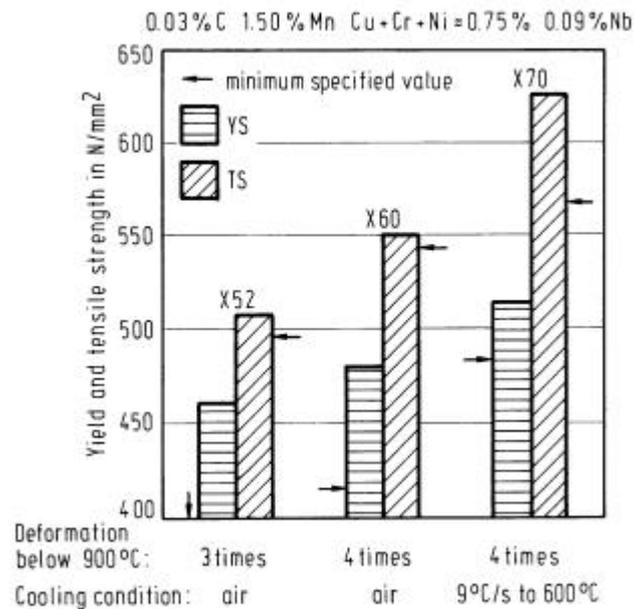


Figure 22. Tensile properties of 22.3 mm plates of HTP steel containing 1.50 % Mn as a function of finish rolling and cooling conditions; finish rolling temperature = 850 °C.

As already indicated in Figure 21, the strength properties are not reduced, when the finish rolling temperature is relatively high in the austenite region. The important condition to obtain high strength and toughness is a high total deformation below the recrystallisation stop temperature, i.e. below 1060 °C. This is, of course, the highest temperature measured and this position is typically in the core of the transfer bar. High temperature processing in combination with accelerated cooling is a very successful plate production method. Results, which have been obtained in trial production of 20 mm plate (17), are given in Table I. Despite the different microstructure, which consists of fine grained ferrite plus some bainite with 800 °C FRT and 100 % bainite with finish rolling at 950 °C, the mechanical properties with regard to both, strength and toughness, are practically identical. The result indicates, that X 70 properties with excellent notch toughness can be achieved, while finish rolling 200 °C higher than usual.

Table I: Properties of accelerated cooled, 20 mm HTP plate (0.03 % C, 1.5 % Mn, 0.10 % Nb)

Finish Rolling Temperature	Rt _{0.5} in MPa	Rm in MPa	CVN Energy at - 100 °C in J
800 °C	496	593	236
950 °C	500	616	277

Hot strip rolling trials confirm the versatility of this alloy design when using accelerated cooling. Trials with 3 to 5 mm material produced yield strength greater than 550 MPa and tensile strengths of more than 630 MPa with typical finish rolling temperature of 880 to 900 °C but combined with a wide range of coiling temperatures, varying from 480 to 610 °C (18). The lower coiling temperatures increase the amount of bainite, whereas the higher coiling temperatures allow more niobium carbides to precipitate. These two different strengthening mechanisms maintain the strength at an equal level for a wide range of coiling temperatures.

This versatility of the HTP alloy design is also illustrated by the results achieved with other trials carried out in a plate mill, where after thermomechanical rolling of a 20 mm plate accelerated cooling with a high cooling rate of almost 60 °C/s was applied (19). In this trial the temperature, at which the fast cooling was stopped, was varied from 650 to 100 °C, covering the processes QST (quenching plus self tempering) at the higher and direct quenching at the lower range of the investigated cooling stop temperatures. The results achieved are presented in Figure 23. At the highest cooling stop temperature (CST) the microstructure close to the surface consists of about 30 % ferrite and 70 % bainite with a change in the volume fraction of these two constituents towards the core of the plate, where the microstructure consist of about 80 % ferrite and 20 % bainite. Even though there is almost no change in the microstructural constituents between a CST of 650 °C down to 550 °C a certain drop in the strength (about 30 MPa in yield strength) is observed. This indicates, that at a higher cooling stop temperature the precipitation of NbC in ferrite becomes more complete. With the increase of the bainite fraction below a 550 °C CST, the strength increases and X 80 properties are achieved with a CST of around 400 °C. With the appearance of some martensite in the microstructure at CST below 350 °C, the yield strength is reduced, while the tensile strength is increased, this is a well known feature of dual phase steel.

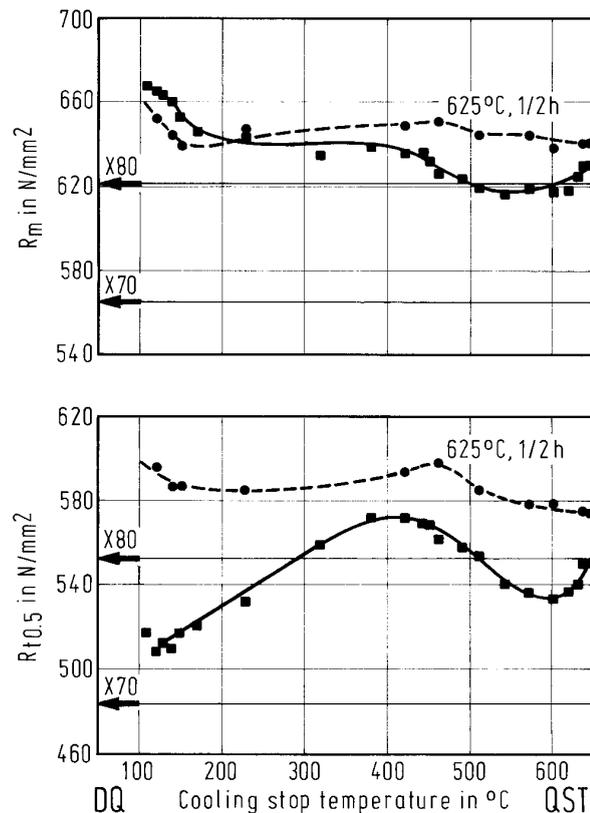


Figure 23: Tensile properties of 'direct quenched' 20 mm HTP plate (cooling rate 60 °C/s) as a function of the cooling stop temperature and after an additional annealing treatment.

When annealing these samples one obtains almost equal properties for all cooling stop temperatures and a gain in yield strength of at least 30 MPa, which indicates that the precipitation hardening potential of niobium has not been used completely in the accelerated cooled condition.

Other Alloying Concepts

It has already been mentioned that in air-cooled HTP plates a higher manganese content is very effective for increasing the strength. This is not only the result of solid solution hardening, but also manganese's role in retarding the γ to α transformation, which gives a further strength increase by refining the ferrite grains and promoting the formation of bainite. These results are presented in Figure 24 and combined with results of HTP plates with higher alloy content (13). In order to combine the effect of the various alloying elements into one alloy factor the constants from a carbon equivalent formula for low carbon steels (20) have been adopted. This figure indicates, that greater amounts of manganese, as well as additions of molybdenum and boron, add to further strength increase especially by promoting the transformation into low carbon bainite. Data exist for investigations with molybdenum-free, boron containing HTP plates indicating that, for such alloy designs, the constant for boron underestimates its transformation retarding effect (21). In order to achieve X 80 properties in air-cooled HTP steel, a rather high alloy factor of around 0.145 is needed. Even though such steel will exhibit excellent toughness after thermomechanical rolling, such high alloy contents may be expected to have a detrimental effect on heat-affected zone properties and from an expense viewpoint accelerated cooling is usually preferred.

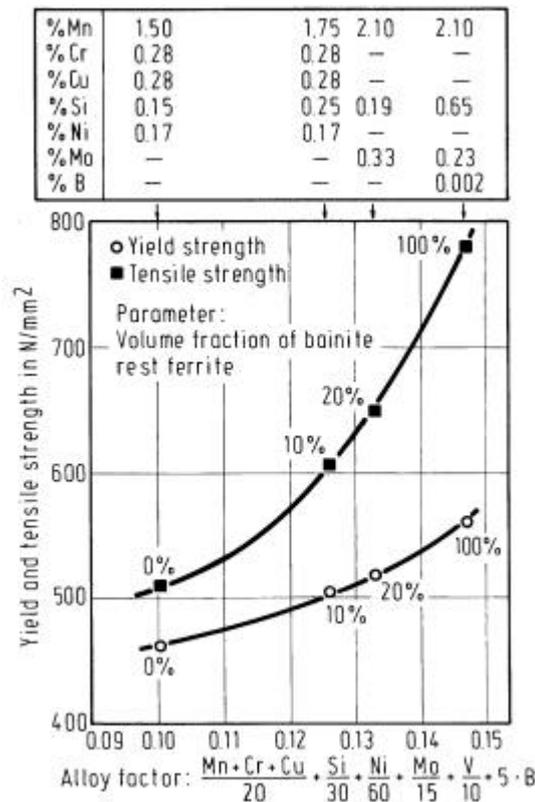


Fig. 24. Tensile properties of air cooled 18 mm HTP plates.

To investigate the sensitivity of the HTP alloy concept to changes in nitrogen and titanium heats with a rather large range of nitrogen levels (0.0032 to 0.0092 %) and titanium contents from 0.008 to 0.024 % were investigated (22). With the exception of one heat all titanium

additions were understoichiometric to nitrogen. The 'free nitrogen', i.e. theoretically not combined as TiN according to the equilibrium condition (23) at 1200 °C, was calculated for each steel composition. Even though this approach may have limitations due to the complex chemical composition of the coarse carbonitrides, the amount of 'free nitrogen' was used to explain the scatter in mechanical properties of these plates. It can be assumed that the 'free nitrogen' will precipitate as 'NbN' on the TiN particles, thereby reducing the solute niobium content in the lower austenite region. Thus, even though all steels had a niobium level in the range of 0.09% to 0.10%, the calculated 'effective' niobium content was reduced to values as low as 0.055%. For identical rolling conditions a good correlation exists between this calculated 'effective' niobium content and the yield strength, Figure 25.

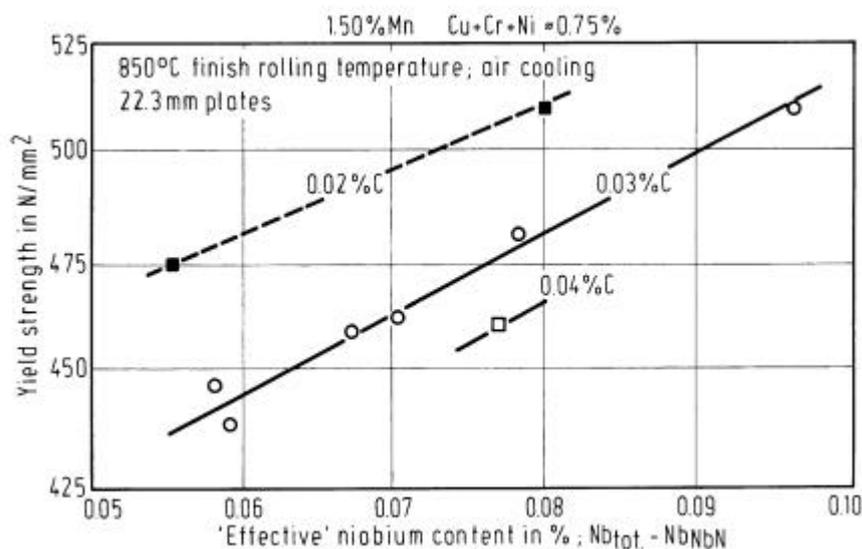


Figure 25: Yield strength of HTP plates considering the influence of carbon, nitrogen and titanium on the effectiveness of niobium.

In addition to the 0.03% carbon plates containing varying levels of nitrogen and titanium, Figure 25 also shows the yield strength data for HTP plates exhibiting slightly higher or lower carbon levels. With lowering of the carbon content a higher yield strength is observed, which may be surprising at first glance. However, this can be explained by the fact, that not only the greater amount of niobium, but also a lower amount of carbon increases the volume fraction of niobium carbides available for precipitation after austenite processing. Furthermore, the larger amount of solute niobium also has a transformation retarding effect, as discussed previously, and so adds to the strength increase. The increase in strength by approaching the stoichiometric ratio of $(Ti + Nb)/(C + N)$ has been observed earlier (23), however it is true only in the case of excess interstitials remaining in the steel. When the stoichiometric composition is exceeded, e.g. by further lowering the carbon content or increasing the niobium content, not only will the theoretically available amount of precipitates be reduced, but also the interstitial free status will itself cause an immediate drop in the tensile properties. This is combined with reduced toughness of the steel owing to weak grain boundaries. Considering segregation in commercial steel, it is therefore recommended not to lower the carbon content much below 0.03%, so as to avoid the risk of reaching the interstitial free condition.

The effect of nitrogen and carbon in lowering the yield strength of air-cooled material, but especially of accelerated cooled material, is shown by comparing steels A (9) and steel B (25) in Figure 26. An optimised HTP steel is based on low nitrogen content and matched with a stoichiometric addition of titanium together with carbon, niobium and the other alloying

elements compatible with the installed rolling and cooling equipment, while keeping cost in mind.

The HTP steel produces excellent properties in thick plate, as shown previously. Additional data are presented in Figure 26, where the 34 mm plate of steel A is compared with the properties of sour gas resistant low manganese plates of the same thickness. The alloy design of this commercially produced steel C (26), is also based on the low interstitial concept in order to reduce dendritic segregation, but using a different combination of the microalloying elements niobium plus vanadium. Additional strengthening of this steel could be achieved by using more niobium or solid solution hardening elements such as chromium either single or in combination.

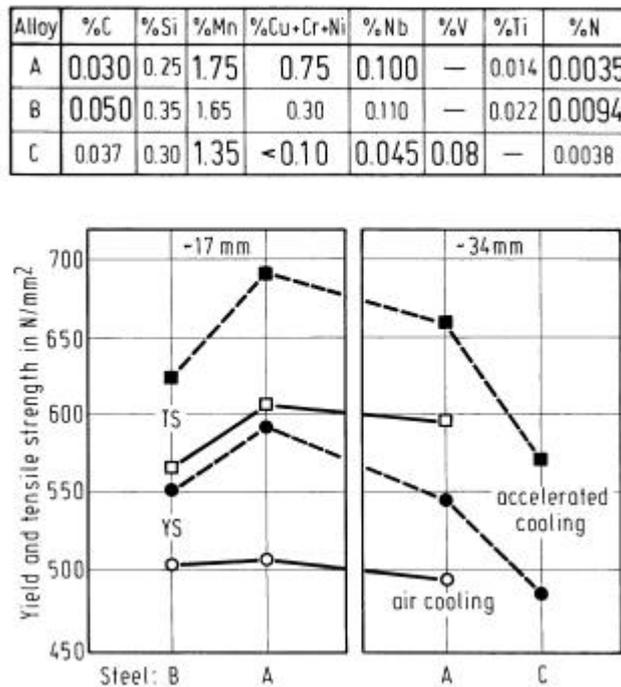


Figure 26: Tensile properties of HTP plates demonstrating the influence of interstitial and alloying elements and cooling conditions.

Weldment Properties

The HTP alloy design produces excellent toughness in the heat affected zone (HAZ), far superior to conventional pipe steel, and for a wide range of cooling rates. This is shown in Figure 27, which presents results of welding simulations (9). The simulated welding cycle represents the conditions in the grain coarsened heat affected zone (GHAZ), which is usually the region of poorest toughness. It consists of a reheat treatment to a peak temperature of 1350 °C, followed by different cooling rates, which were measured between 800 and 700 °C during the cooling process. The data in Figure 27 include the most commonly applied commercial welding processes for pipelines, such as manual metal arc welding (MMA)- often applied in pipe laying in the field - with a cooling rate of about 100 °C/s or in the submerged arc welding process (SAW) having a cooling rate of about 10 °C/s, which is the standard process for large diameter pipe production and double jointing. The study shows, that the impact properties in the HAZ of HTP steel are far superior to these obtained in a conventional ferritic-pearlitic pipe steel X70, which are based on a higher carbon content leading to a peritectic transformation during solidification. Even when welding processes with much lower cooling rates are applied,

such as electro slag welding (ESW), satisfactory toughness can be expected in the HAZ of the HTP steel. A slow cooling rate of about 1 °C/s can be expected also in the flash butt welding process (FBW), which is applied for field welding in the CIS.

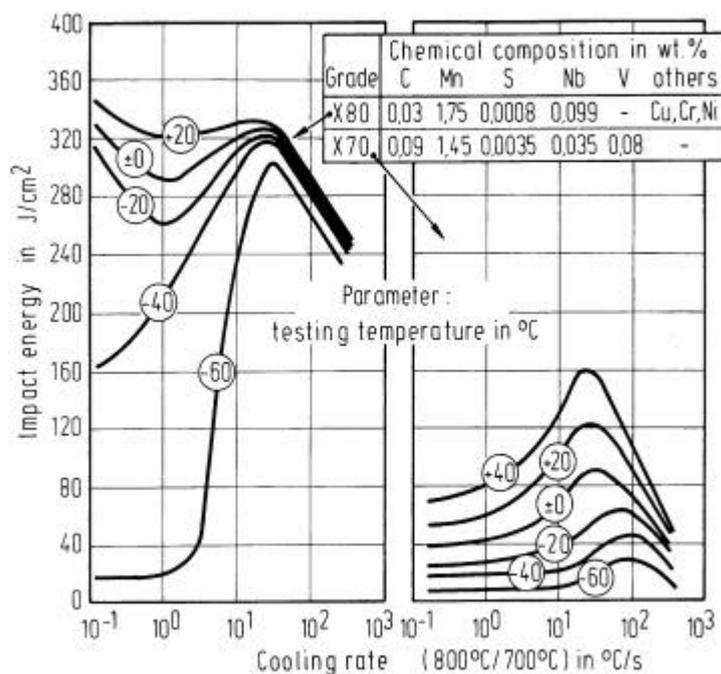


Figure 27: Charpy -V – notch impact energy of two pipe steels in the grain coarsened heat affected zone; welding simulation with a peak temperature of 1350 °C.

The excellent toughness for a wide range of welding processes is attributable to the formation of low carbon bainitic microstructures over a wide range of cooling conditions, Figure 28. It should be noted that even for the relatively fast cooling rate typical for field welding no martensite is formed in the GHAZ.

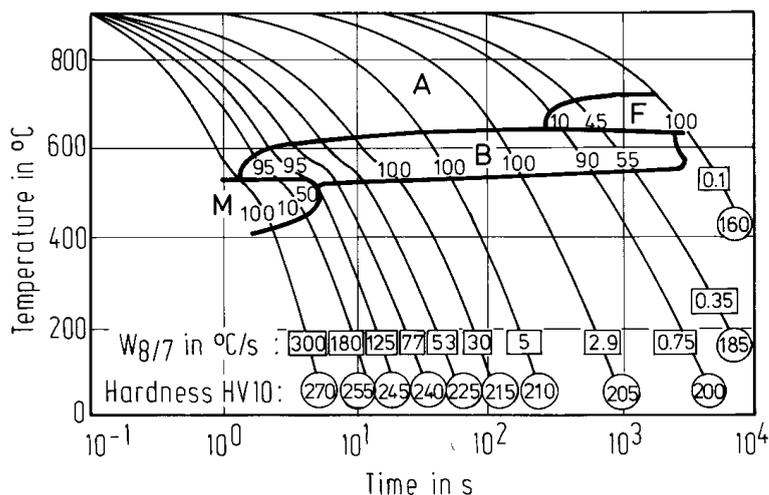


Figure 28: Transformation behaviour for simulated HAZ (peak temperature 1350 °C) of HTP steel with 0.03 % C – 0.10 % Nb and 1.75 % Mn.

The HAZ toughness, microstructure and CCT diagram of the HTP steel with the lower manganese content of 1.50 % Mn are very similar to those the 1.75 % Mn steel (27). This observation is in agreement with a model shown in Figure 29 (28), which has been developed

from studying the weldability of a wide variety of low carbon HSLA steels with different chemical compositions. At a first glance it is surprising, that higher alloy contents in low carbon steels can have a positive effect on toughness in the grain coarsened heat-affected zone. However at higher alloy contents the transformation occurs at lower temperature and thus finer acicular microstructures replace coarse and granular microstructures. Nevertheless, there exists an optimum alloy content for each cooling rate, since at very high alloy contents the microstructure will contain martensitic constituents, which have a detrimental effect on toughness. The 0.03% carbon steels in Figure 29 having above optimum alloy content were designed to produce X80 without accelerated cooling, but relying on larger amounts of alloying elements, such as combinations of 2% manganese plus molybdenum and boron. Therefore besides economic considerations the ease of weldability make accelerated cooling more favourable.

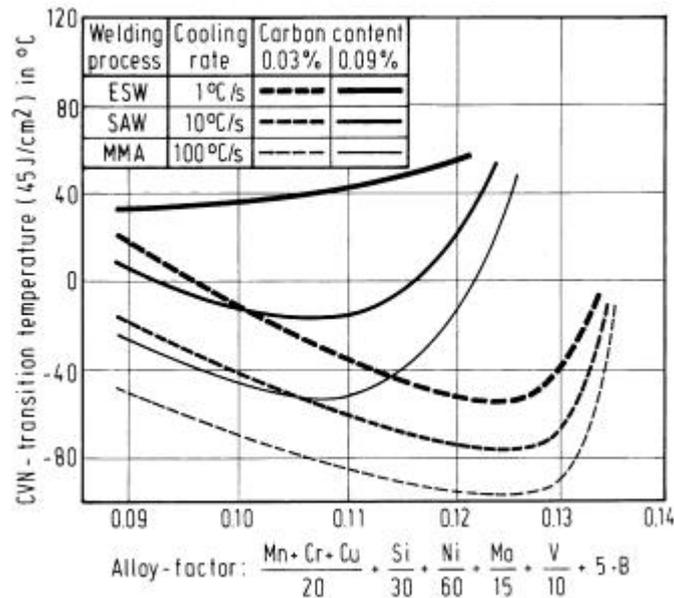


Figure 29: Impact toughness of simulated heat affected zone (peak temperature = 1350 °C) as a function of alloy content.

The worst welding condition with regard to weldment properties exists in the FBW process, due to the relatively long processing time and high heat input, which causes a wide heat affected zone. This gives a substantial drop in tensile and impact properties (HAZ softening), which may disqualify the process or will need post weld treatment such as induction heating, quenching and tempering to recover the lost strength. In a major study to classify various pipe steels for the flash butt welding process, the HTP steel was found to be rather resistant to HAZ softening and superior to all the other steels investigated (29, 30). At the testing temperature of -40 °C all other pipe steels showed a wide scatter of impact energies in unnotched specimens with data as low as 10J, but the HTP steel always produced more than 300 J impact energy. The lowest hardness and strength results are observed at a distance of 30 to 40 mm from the fusion boundary, Figure 30, where the peak temperature is in the intercritical region a+?. The actual strength values are about 50 to 100 MPa higher than for other pipe steels investigated and reached X 65 properties. To restore the original X 70 properties a heat treatment is recommended, which requires reheating to 1100 °C followed by accelerated cooling.

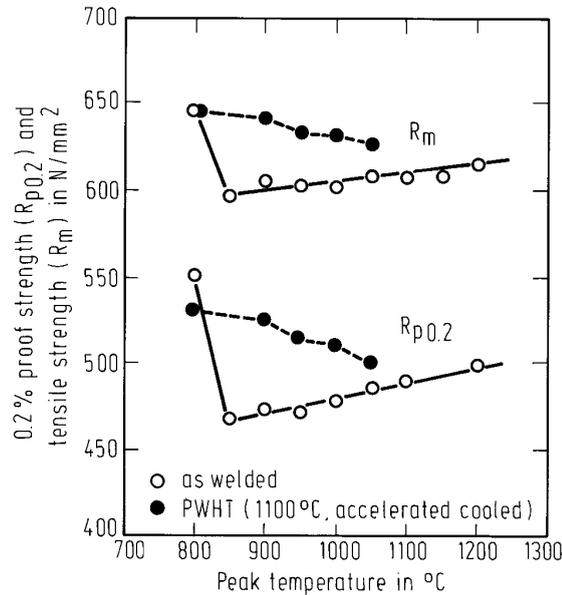


Figure 30: Tensile properties of a flash butt weldment.

Properties in the weld metal depend on the consumables and the chemical composition of the base metal due to dilution effects. For multi-layer weldment by the MMA process the base metal is of minor importance due to the low dilution factor, whereas about 60% of the base metal is dissolved in the SAW. Thus the consumables for HTP steels must be suitable to tolerate a niobium content of about 0.06 %. The best results are achieved with a wire giving a low carbon bainitic microstructure (Mo, Ti and B containing) in combination with an alumina basic flux to guarantee low oxygen contents (9). Even so for the second seam the niobium-carbide precipitation will be more complete, resulting in a certain hardness increase in this region, the absolute value will nevertheless remain below the 250 HV level.

Application of the HTP Concept

The concept of pearlite free steel with low carbon (<0.02 %) including the positive role of niobium up to 0.11% was described thirty years ago (31). Furthermore, a steel based on 0.04% C, 1.60% Mn, 0.25% Mo and 0.06% Nb was already produced by IPSCO and successfully applied by the TransCanada PipeLine Company Ltd. for a major expansion project in 1971/72 (32). Based on this first use of the 'acicular ferrite' concept several steel companies in North America, Europe (Italy, France) and Japan carried out research work and had industrial production. Also the positive role of accelerated cooling and quenching has already been described (33).

Nevertheless the low carbon bainite alloy design declined in importance with the molybdenum crisis at the end of the 1970's, although it was still used by IPSCO. Therefore the polygonal ferrite, pearlite containing, niobium plus vanadium microalloyed steel became the most relevant grade for line pipes, especially for X 70. With the results of the demonstration heat (9) one decade later the interest in this concept of a low carbon bainitic pipe steel was reintroduced for selected applications, especially since the possibility of high temperature thermomechanical rolling could be demonstrated and an acicular microstructure could be obtained without molybdenum additions.

Economical hot strip production naturally utilizes a higher finish rolling temperature than plate production, to accommodate the high deformation per pass in the continuous rolling process of

the finishing train. Therefore often higher niobium levels are observed compared to pipe plate of the same strength and thickness (34). It has been demonstrated, that a 0.05 %C + 1.85 %Mn + 0.30 %Cu + 0.30% Cr + 0.20 %Ni + 0.09 %Nb + 0.03 %V steel gives excellent X 80 properties in spiral pipe of 16 mm wall (35). A more recent pipe plate order for 45,000 tons of X80 also followed this concept (36). This particular plate mill utilized a modest accelerated cooling system producing a cooling rate of 4 °C/s, therefore the steel had to rely also on a molybdenum addition. The typical chemical composition was 0.05 %C + 1.75 %Mn + 0.30 %Cu + 0.30 %Ni + 0.30 % Mo + 0.08 % Nb + 0.01 % Ti.

In contrast to the strong mills in Europe, Korea and Japan, in North America several older plate mills exist, which do not accommodate high rolling loads and therefore need to operate at higher rolling temperatures. There the HTP concept has been frequently applied in recent years after tailoring to local conditions. Pipe steel production in Steckel mills may also require higher temperature processing conditions. This requirement is traceable to the need to coil the sheet bar during the final rolling processing. Thus high temperature processing offers the opportunity for these companies to produce thermomechanically rolled pipe steel. The total tonnage of HTP steel produced in the last decade surpassed already the threshold value of one million tons.

Another interesting application is in clad pipe, where the required corrosion resistance of the high alloy cladding material does not allow application of low finish rolling temperatures. The highest corrosion resistance of the cladding material is obtained in the solution treated condition, but it can also be realized in the as rolled condition by direct quenching, when no major intermetallic precipitates are formed before the quenching operation. The critical pitting temperature for the commonly applied Incoloy 825 is favourable only when a finish rolling temperature above 950 °C and at least three minutes delay time before quenching are applied, Figure 31 (37). Lower finish rolling temperatures or shorter delay times reduce the effectiveness of the cladding. On the other hand the HSLA steel substrate has to exhibit the strength, toughness and field weldability of pipeline steel, which is traditionally possible only with thermomechanical rolling. Data obtained by two companies are summarized in Table II. By substituting their conventional low carbon alloy with a high niobium HTP steel for the clad pipe production an improvement of 20 °C in the BDWTT transition temperature has been achieved.

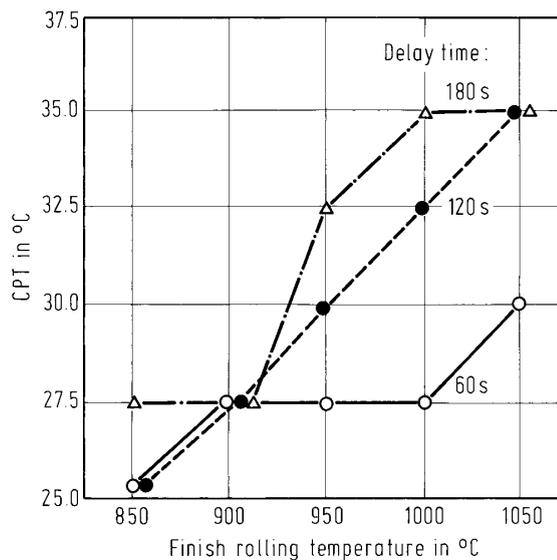


Figure 31: Effect of finish rolling temperature and delay time before direct quenching on the critical pitting temperature of Incoloy 825, test method according to ASTM G 48, 48 hours.

Table II Chemical composition of the base metal and mechanical properties of clad pipe

Reference	Steel type	% C	% Mn	% Cu+Cr+Ni+Mo	% V	%Nb	%Ti
37	Conventional	0.04	1.43	0.36	0	0.04	0.01
37	HTP	0.04	1.54	0.27	0	0.09	0.01
34	Conventional	0.04	1.52	0.41	0.05	0.03	0.03
34	HTP	0.04	1.5	0.33	0	0.1	0.01

Reference	Steel type	YS (MPa)	TS (MPa)	85 % shear BDWTT °C
37	Conventional	524	592	3
37	HTP	539	603	-18
34	Conventional	478	575	0
34	HTP	516	612	-18

Summary and Conclusions

The processing–microstructure-property relationships for steels employing the HTP concept were evaluated for 0.03% carbon – 0.10% niobium steel, utilizing various alloy designs and different rolling practices. The benefits of this approach include the possibility of finish rolling at a temperature about 100 to 200° C higher than that for conventional thermomechanical rolling, while maintaining excellent toughness, ductility and welding as well as minimizing segregation of all alloying elements. These steels are thus being favoured, when sour gas resistance is also required.

The optimum microstructure is a low carbon bainite, which can be obtained by accelerated cooling or additional alloying. Furthermore the precipitation hardening potential of NbC can also be maximised. These complementary effects are summarised in the nomograph Figure 32 by reference to niobium in solid solution at the finish rolling temperature.

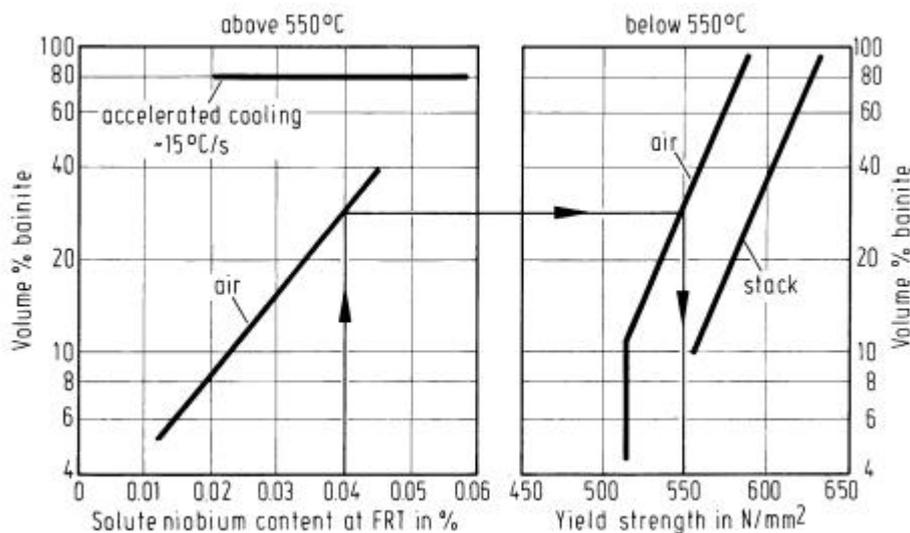


Figure32: Effect of solute niobium and cooling conditions on microstructure and yield strength of HTP Nb steel.

The HTP concept has been adapted to the available facilities in various companies. In order to obtain the necessary yield and especially the necessary tensile strength for X 70 pipes a volume fraction of about 20% bainite is needed in these low carbon steels. This can be obtained by

increasing the alloy content or increasing the cooling rate after thermomechanical rolling. The niobium content in this alloy design adds to strength increase not only by facilitating high temperature austenite conditioning but also by causing the γ to a transformation to occur at a lower temperature (which results in a higher volume fraction of bainite) and by coherent ferrite precipitates. In order to make optimum use of the niobium addition low carbon contents (typically 0.03 %), a low nitrogen content (below 50 ppm), and a stoichiometric addition of titanium to nitrogen are recommended. By increasing the volume fraction of bainite with the above mentioned means, even thick wall sour gas resistant pipes of grade X 80 becomes possible.

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